

Liquid-Crystalline Assemblies Containing Ionic Liquids: An Approach to Anisotropic Ionic Materials

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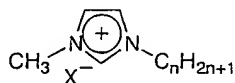
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Amphiphilic ionic liquid derivatives form self-organized lamellar liquid crystals with room temperature ionic liquids. The ionic conductivities along the smectic layers have been obtained for the samples aligned in the cells with electrodes. The highest value is $4.3 \times 10^{-2} \text{ S cm}^{-1}$ at 139 °C.

Liquid crystals combine order and mobility in molecular and supramolecular levels.^{1,2} The control of the molecular alignment and the organized structures in the liquid-crystalline states can lead to the introduction of anisotropic functions for the organic optoelectronic and ion-conductive materials.³ Recently, organic ionic liquids have attracted attention as electrolytes⁴ and solvent media⁵ for reactions and extractions because of their specific properties such as ion-conductive, non-volatile, and catalytic properties. Here, we intend to obtain anisotropic ion-active materials through self-organization of ionic materials. It has already been reported that ionic liquid derivatives having long alkyl chains alone show thermotropic smectic liquid crystallinity.⁶ If these amphiphilic molecules can form the liquid-crystalline organized structures with ionic liquids, their ionic assemblies would be expected to function as anisotropic materials exhibiting high ionic conductivities. Their physical properties may also be easily tuned by the fraction of ionic liquids in the mixtures.

We report here a new class of self-organized systems, which is obtained by mixing of imidazolium ionic liquids and its amphiphilic derivatives having an octadecyl alkyl chain, as shown in Figure 1. The ionic conductivities of the self-organized materials have been examined.



1a: X = BF₄, n = 18 2a: X = BF₄, n = 2
1b: X = PF₆, n = 18 2b: X = PF₆, n = 4

Figure 1. Structure of 1-methyl-3-alkylimidazolium salts.

Two room temperature ionic liquids 2a and 2b, which have hydrophilic and hydrophobic counter anions, respectively, have been selected to examine the ionic effects on the self-organization behavior for the amphiphilic molecules 1a and 1b. These compounds are prepared by N-alkylation of 1-methylimidazole with 1-bromoalkane, followed by the metathesis reaction using HBF₄ or HPF₆ aqueous solution.⁶

Figure 2 presents a phase diagram for the binary mixture of 1a and 2a as a function of the mole fraction of 2a. Compound 1a alone forms the thermotropic smectic A (S_A) and higher ordered

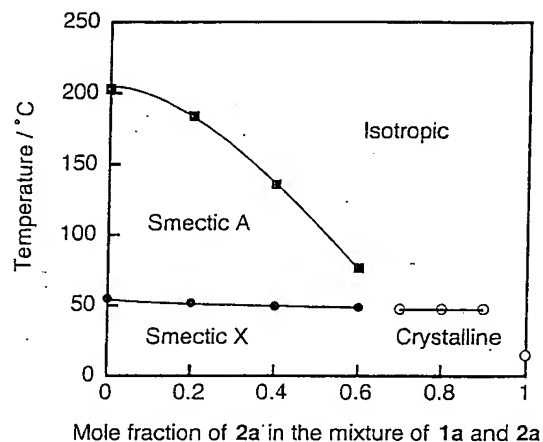


Figure 2. Phase transition behavior for the mixture of 1a and 2a on the heating runs.

smectic phases (S_X). For the mixtures of 1a and 2a, these smectic phases are observed up to the mole fraction of 0.6 for 2a in the mixture. The isotropization temperatures are greatly decreased with the increase of the fraction of 2a. The mixtures having more than the mole fraction of 0.7 of 2a show no liquid crystallinity. For the mixture containing the smaller fraction of 1a (0.5 wt%), the weak translucent gel is obtained below 50 °C.⁷ Under polarizing microscopy, optically anisotropic fibrous aggregations are observed in the isotropic ionic liquid. For the mixtures consisting of 1b and 2b, no smectic liquid-crystalline phase is seen more than the mole fraction of 0.4 of 2b.

Ion-conductive properties have been examined for compound 1a alone and the self-organized mixture of 1a and 2a, which form the smectic liquid-crystalline phases.⁸ A glass plate with comb-shaped gold electrodes (Au) and a pair of indium tin oxide (ITO) electrodes are employed for the anisotropic measurements of the ionic conductivity.^{3f} For the samples forming the S_A phase, a homeotropic alignment is achieved on the glass surface with gold electrodes, which has been confirmed by polarizing microscopy, as schematically illustrated in Figure 3a. In this case, the ionic conductivities (σ_{\parallel}) along the direction parallel to the smectic-layer plane are measured for the aligned samples. In contrast, for the ITO electrodes, the ion-conductive values (σ_{\perp}) along only direction perpendicular to the smectic-layer plane are not obtained because of polydomain formation, as illustrated in Figure 3b.

Figure 4 shows the ionic conductivities of compound 1a and the mixture of 1a and 2a in the molar ratio of 3 : 2 (1a/2a = 3/2) as a function of temperature. The ionic conductivities for the samples homeotropically aligned in the S_A phases are higher than

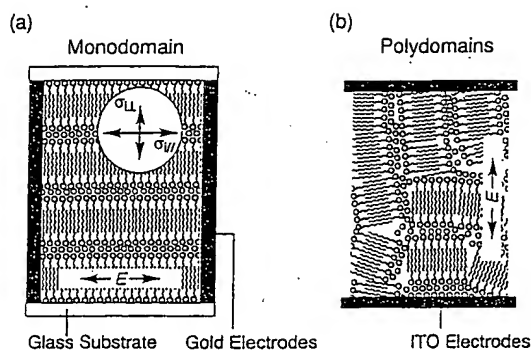


Figure 3. Schematic illustrations of the smectic liquid-crystalline ionic assemblies aligned with monodomain (a) and polydomains (b) on the glass surface with gold electrodes and on the ITO electrodes, respectively. E : Electric field.

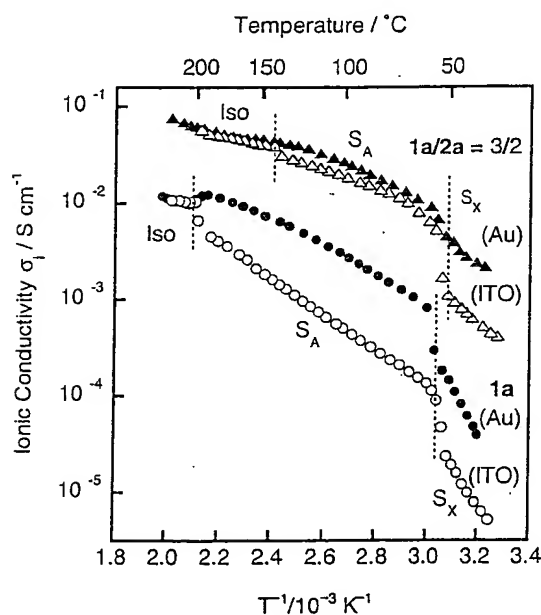


Figure 4. Ionic conductivities for the smectic liquid-crystalline samples of 1a alone and 1a/2a, which are aligned with monodomain (●, ▲) and polydomains (○, △) on the glass surface with gold electrodes and on the ITO electrodes, respectively.

those for the samples with polydomains. When the liquid-crystalline order disappears at the isotropization temperatures on heating, the ionic conductivities for the samples filled in the both cells with Au and ITO electrodes show no difference due to the disorder of the mixture. The formation of anisotropic long-range conductive pathways in the homeotropically aligned S_A phases should contribute to high ionic conductivities. The incorporation of mobile simpler ionic liquid into these pathways enhances the ionic conduction in the layered structures. The $\sigma_{i//}$ values for the homeotropically aligned mixture forming the S_A phase become

about 10 times higher than those for 1a alone.

It was reported that the ionic conductivities of isotropic ionic liquids alone gradually increase with the increase in temperature.^{4b} In contrast, for the mesomorphic materials in the present study, the discontinuous changes of ionic conductivities are observed at the phase transitions. For example, the ionic conductivities ($\sigma_{i//}$) for the aligned sample of 1a increase at 55 °C and decrease at 203 °C on heating. These temperatures correspond to the S_X - S_A and S_A -Isotropic (Iso) transitions, respectively. The isotropic ionic conductivity of the single component of 2a at 30 °C is $2 \times 10^{-2} \text{ S cm}^{-1}$,⁹ while the anisotropic ionic conductivity ($\sigma_{i//}$) of 1a/2a in the molar ratio of 3:2 is $2 \times 10^{-3} \text{ S cm}^{-1}$ at the same temperature. It is noteworthy that the liquid-crystalline assemblies keep relatively high ionic conductivities even though insulating aliphatic layers are incorporated.

Amphiphilic ionic molecules presented here form the self-organized lamellar liquid crystals with room temperature ionic liquids. These liquid crystals are novel functional materials, which show anisotropic ion-active properties. The ionic conductivities of the organized materials are tunable by the change of the fraction of ionic liquids.

References and Notes

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